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学 位 論 文 題 名

Advanced XAFS analysis for local structure of functional materials

(先端 XAFS 解析の開発と機能性物質の局所構造)

X-ray absorption fine structure (XAFS) provides bond distance, type of atom, coordination number around the X-ray absorbing atom. Therefore, it is suitable to determine the local structure of the compounds. For example, precision catalysis is of particular importance of emerging technologies to enhance the selectivity and efficiency for one interested application. Precision catalysis requires a synthesis with atomic-level precision because a difference of only one atom causes significant change in their reactivities and properties. Not only is synthesis an essential for the precision catalysis but also the analysis method to determine the structure precisely. Metal containing compound have drawn much interest because of their wide applications such as gas reforming, fuel cell. Local structure especially of metal and its neighbor is the key to develop precision catalysis, however, widely used analysis methods provide not enough local structural information. XAFS is the most suitable technique to identify its local structure. But there are still three problems that hinder the exact XAFS analysis on the material. 1. One dimensional structure analysis, 2. Limited Fitting parameters 3. Difficulty in Low-Z element operando analysis. In this study, I shall investigate the local structure of various systems which show unique properties, but it is difficult to obtain its structure due to the above mentioned problems. In addition, I demonstrate the evidence which might lead to the brand-new type of XAFS called MARX-Raman. The thesis is composed of 6 chapters to describe my contributions to new development in XAFS techniques.

Chapter 1 is the introduction and background of the study.

In Chapter 2, the general experimental procedure is described.

In Chapter 3, I describe a method for determining the three-dimensional structure of supported metal catalysts. Supported metal catalysts have drawn much attention for their wide applications such as catalysts, sensors, electronic and magnetic devices. It is very important to control the structure and electronic state of the supported metal, including the metal cluster size. Metal oxides are widely used as substrates for preparing highly dispersed metal clusters with their size less than a few nm. To investigate the metal-metal oxide interaction, a well-defined single crystal metal oxide is needed as a model substrate. In addition, an analysis method capable of providing three-dimensional structural information of the surface species is essential. Polarization-dependent X-ray absorption fine structure (PTRF-XAFS) analysis can uniquely provide such information around highly dispersed metal species on single crystal surface. In this study, Ni and Pt were deposited on $\text{TiO}_2(110)$ surfaces premodified with ortho-mercaptopbenzoic acid (o-MBA). The PTRF-XAFS results indicate that Ni were atomically dispersed on $\text{TiO}_2(110)$ surface by forming S-Ni-O bonds (where the S is of o-MBA and O is of TiO_2). Bent S-Ni-O were formed, and its angle were estimated to be 156° . On the contrary, Pt were aggregated

to form small clusters.

In Chapter 4, I talk about XAFS applications to the unique compound (the gold (I) complex, $[(C_6F_5Au)_2(\mu-1,4\text{-diisocyanobenzene})]$ (1)) (JACS, 2008 130 100044). The compound undergoes the reversible color change from blue to yellow by mechanical treatment (mechanochromism), the origin of which remains unknown. The mechanochromism draws a lot of interest because it can be used as recording and sensing materials. The origin of the color change was postulated to be due to the creation of Auophilic interaction. However, the ground Au complex structure remained unknown because of its amorphous structure. We have applied XAFS to get the local structure of Au. We found Auophilic interaction in the ground crystal (1) at 0.287 nm which might be the origin for the mechanochromism.

In Chapter 5, I report the evidence that might lead to the brand-new kind of spectroscopy. XAFS that has been used in the aforementioned provides invaluable local structural information. Since the X-ray has a large penetration ability, it is possible to carry out an in situ measurement of catalysts and electrodes under reaction conditions. However, when applied to low Z elements, which have an X-ray absorption edge in the soft X-ray regime, it is quite difficult to observe the XAFS under the reaction conditions. On the other hand, X-ray Raman scattering (XRS) can provide in situ XAFS measurements on low Z elements because the XRS uses hard X-rays. However, the X-ray Raman intensity is quite low. Resonant XRS is observed and enhances the Raman sensitivity. In this resonant XRS, the X-ray is tuned to the absorption edge and the Raman signal of the same X-ray absorbing atom is detected. Therefore, the X-ray absorption and Raman emission occur at a single atom. If one uses an absorption edge of the central metal in a metal complex to which low Z atoms are directly coordinated and if the excitation energy transfer occurs from the X-ray absorbing atom to the coordinating low Z atoms, one can obtain the X-ray Raman spectrum of the directly bonded low Z atoms, which is enhanced through the X-ray absorption of the central atom. In this study, the interatomic resonant Raman signal were measured by tuning the X-ray to the excitations of Ta L_3 -edge and Er L_1 -edge with the detection of Raman emission of N K-edge and C K-edge, respectively, in order to see such an enhancement occurs or not, qualitatively. When the excitation X-ray energy was tuned to the Ta L_3 -edge and inelastic scattering spectra were recorded around 400 eV loss corresponding to the N K-edge Raman region, we found a clear enhancement of emission spectrum. The same enhancement was observed in C K-edge Raman region in $Er(C_5H_5)_3$. These experimental results indicated the possibility of MARX-Raman phenomenon which may lead to a new in situ and bond-specific XAFS spectroscopy for low Z elements.

Chapter 6 is conclusion. XAFS methods are able to determine local structure around metal and provide the local structural information precisely. Moreover, the new possible phenomena I found that might lead to the development of new kind of spectroscopy are introduced. These works have greatly contributed to XAFS spectroscopy and material science.